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Time resolved strain dependent morphological study of electrically conducting nanocomposites

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Time resolved strain dependent morphological study of electrically conducting nanocomposites

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Abstract. An efficient and reliable method is introduced to understand the network behaviour of nano-fillers in a polymeric matrix under uniaxial strain coupled with small angle x-ray scattering measurements. The nanoparticles (carbon nanotubes) are conductive and the particles form a percolating network that becomes apparent source of electrical conduction and consequently the samples behave as a bulk conductor. Polyurethane based nanocomposites containing 2% w/w multiwall carbon nanotubes are studied. The electrical conductivity of the nanocomposite was ($3.28x10^{-5}$s/m).The sample was able to be extended to an extension ratio of 1.7 before fracture**.** A slight variation in the electrical conductivity is observed under uniaxial strain which we attribute to the disturbance of conductive pathways. Further, this work is coupled with in-situ time resolved small angle x-ray scattering measurements using a synchrotron beam line to enable its measurements to be made during the deformation cycle. We use a multi-scale structure to model the small angle x-ray data. The results of the analysis are interpreted as the presence of aggregates which would also go some way towards understanding why there is no alignment of the carbon nanotubes.

1. Introduction

The synthesis and fabrication of nanometer-sized particles has reached a mature state and they can be made with controlled composition and size [1]. Nanoparticles offer high surface area to interact with polymer phase due to which a new interphase develops. Such interphases play a key role in developing the microstructure of the nanocomposite material. The microstructure changes which take place in the nanocomposite, under different conditions ranging from temperature, pressure and mechanical deformation have not been properly investigated. Moreover, nanoparticles in a polymer matrix represent a more dynamic system that has greater freedom for reversible nanoscale restructuring, which is essential for stretchability [2]**.** A disturbance in a multi wall carbon nanotube (MWCNT) network can also disturb the microstructure of the nanocomposite material and consequently the physical properties are altered [3]. Miao and his co-workers examined the piezo resistive response of CNT–polymer nanocomposites and reported a decrease in electrical conductivity [4]. Highly stretchable conductive polymer composites with MWCNT and carbon nanospheres subjected to mechanical strain using polyurethane as the matrix material exhibited an increase of the electrical conductivity of the nanocomposite by 20% under strain, followed by a decrease in conductivity upon further elongation [5]. Such studies suggested that there is a significant effect on electrical conductivity during deformation. These may well reveal structural information about the percolating network. Small angle x-ray scattering (SAXS) is a versatile technique to probe the structure, orientation and network of nano scale particles within a matrix material.In this work, we present small angle x-ray scattering (SAXS) coupled with four probe method to simultaneously measure electrical conductivity to understand the MWCNT network and its behaviour under uniaxial deformation.

2. Materials & Methods:

The carbon nanotubes (MWCNT) purchased from Sigma-Aldrich, Portugal. Commercially available Diphenylmethane diisocyanate, polyol and Dimethyl sulphoxide (DMSO) were used without further treatment. Thermoset polyurethane samples were prepared with 1:1 ratios. figure 1 gives a schematic of the steps in the synthesis of the nanocomposites. The electrical conductivity is measured using a four probe method coupled with tensiometer to enable measurements during deformation as shown in figure 2. The SAXS detector was mounted at a sample-to-detector distance of 6.3m which provides a q range of 0.001 - 0.020 $Å^{-1}$, using a beam of wavelength 1Å.

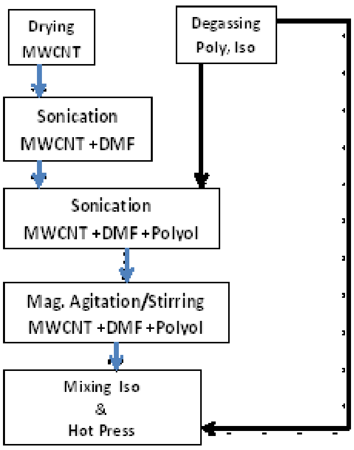

Figure 1. The nanocomposite synthesis mechanism

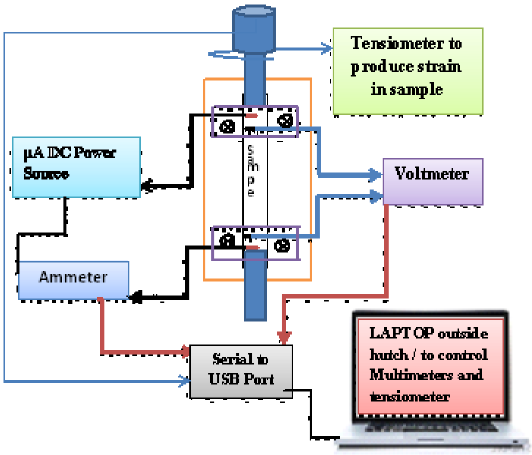

Figure 2. The four probe set up coupled with the tensiometer used in the time resolved SAXS experiment described in the text.

3. Results and Discussion:

3.1 Electrical Conductivity under uniaxial strain:

The measured electrical conductivity (**σ**) with extension ratio λ is plotted in figure 3. The overall electrical conductivity change with extension ratio is slight and shows a decreasing behavior from $3.07x10^{-5}$ s/m to $2.70x10^{-5}$ s/m. The SAXS data was used to evaluate the level of preferred orientation $\langle P_2 \rangle$of the MWCNTs which at its maximum was found to be 0.02. (1.0 corresponds to perfect common alignment and 0.0 to random alignment). The fluctuations in electrical conductivity under uniaxial strain lead to slight decrease in magnitude. The same kind of behavior was reported by Shang and his coworkers in which a nanocomposite was stretched up to 100% without significant variation in electrical conductivity [6]. The electrical conductivity initially increases from $3.07x10^{-5}$ s/m to $3.28\ x10^{-5}$s/m for an extension ratio (λ) of 1.04 and then decreases to $2.80x10^{-5}$s/m. We attribute the decrease in electrical conductivity to be caused by a strained network leading to breaking of certain MCNT contacts. An increase and decrease in electrical conductivity at 20.0% strain was also reported in literature [5]. This is also most likely caused by MWCNT reorganization and stretching under uniaxial strain causes in breaking and relaxation of certain networks to increase and decrease electrical conductivity. The fluctuations in electrical conductivity continue until λ=1.37. A further decrease in electrical conductivity results in breaking of more number of contacts between MWCNT while an increase in electrical conductivity is due to new contact formation. Since, the polyurethane matrix is elastic and can be stretched while MWCNT are rigid and retain their position. These contacts breaking and formation is locally, but when they are significant in number, they will have a global effect.

Electrical conductivity continuously decreases for λ=1.37-1.41 and attains a value2.78x10^{-5} s/m. When λ exceeds a value of 1.41 to 1.45, the electrical conductivity remains constant. An equal number of contact breaking and formation lead towards a minute change in electrical conductivity or either no change at all. An increasing behavior in electrical conductivity is observed for value of λ between 1.45 and1.47 and σ reaches 2.99x10^{-5} s/m and after that till the value of λ=1.55, **σ** remains constant. The initial increase-decrease behavior in **σ** again comes into play with a final value 2.70x10^{-5} s/m till $\lambda_{max.}$ =1.70. The sample is stretched up to 70% of original length. The maximum electrical conductivity (3.30x10^{-5} s/m) is observed for λ=1.22 i.e when sample was strained 22% of original length while minimum electrical conductivity was 2.66x10^{-5} s/m for λ=1.63. In figure 3 the arrows are used to indicate fluctuations in electrical conductivity with respect to the extension ratio while the trend line indicates an overall deceasing trend in electrical conductivity. The decrease in electrical conductivity is consistent with theoretical modelling [7] as well as other reported experimental results under strain [4].

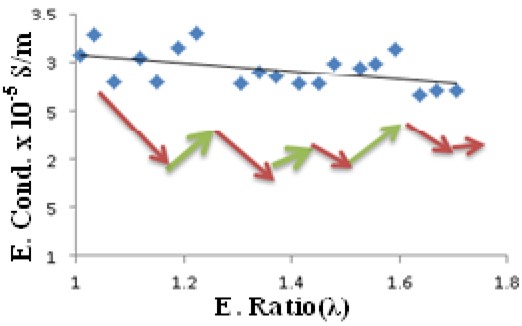

Figure 3. Variation in electrical conductivity vs the extension ratio λ. The red arrows indicate a decrease and green arrows an increase in electrical conductivity while length indicates the magnitude of change

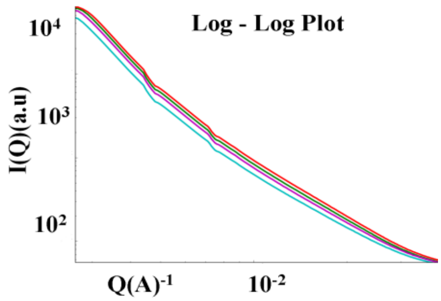

Figure 4. The SAXS curves I(q) plotted on a log-log scale as function of q for samples held at the extension ratios λ=1.45 (green), 1.55 (red), 1.59 (cyan), 1.70 (magenta).

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3.2 Morphology of nanocomposite under uniaxial strain:
SAXS 1-D patterns were obtained by integrating the 2D SAXS images over the azimuthal angle and these are shown in figure 4. The data comes close to a power law curve with an exponent of between 2 and 3. We interpret this as the scattering arising from aggregates or mass fractals lying between disks and spheres. The variation in the value of the slope is associated with a variation in microstructure caused by the disturbance produced by stretching of network of MWCNT which leads to a decrease in electrical conductivity. It is clear that the curve cannot be described using a single structural scale and so we have employed a multiple scale model with aggregates clustered around different dimensions. This is described in the next section.

4. Model:
An empirical unified Power law and R_g Model with level 3, developed by G. Beaucage [8] is used to fit the integrated SAXS data (figure 5). The empirical expressions are used to approximate the scattering from different type of fractal structures. The empirical fit function is

$$I(q) = Bkgd + \sum_{i=1}^{N} G_i \exp\left(-q^2 R_{g,i}^2/3\right) + \frac{B_i\left[erf(qR_{g,i}/\sqrt{6})\right]^{3P_i}}{q^{P_i}} \quad ....(1)$$

	Table 1								
Data	λ	Rg1	Rg2	G1	G2	B1	B2	P1	P2
S_TB3c_0015_out.txt	1.15	20118	757.1	5.44E+05	3.41E+03	2.87E-01	9.26E-05	1.43658	2.641311
S_TB3c_0023_out.txt	1.450058	15783	819.6	4.37E+06	4.93E+03	5.86E-03	2.89E-05	1.931631	2.850562
S_TB3c_0026_out.txt	1.555911	18987	805.4	1.39E+06	5.46E+03	1.37E-01	5.31E-05	0.432537	2.74713
S_TB3c_0030_out.txt	1.7	12904	760.6	4.59E+06	2.64E+03	4.64E-03	3.05E-05	2.139953	2.817482

The parameters, in Table1, are obtained using the empirical model (eq.1) to fit the SAXS experimental data. All parameters from Table1 are directly or indirectly related to microstructure of nanocomposite. In figure 6, we show the radius of gyration (Rg_1) of the largest aggregates which fluctuates and reduces slightly with uniaxial strain as does the smaller scale structures with Rg_2.

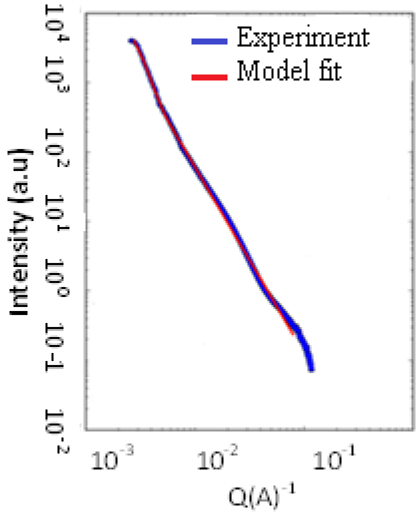

Figure 5. A Comparison of the experimental SAXS data and the Unified model fit (equation 1)

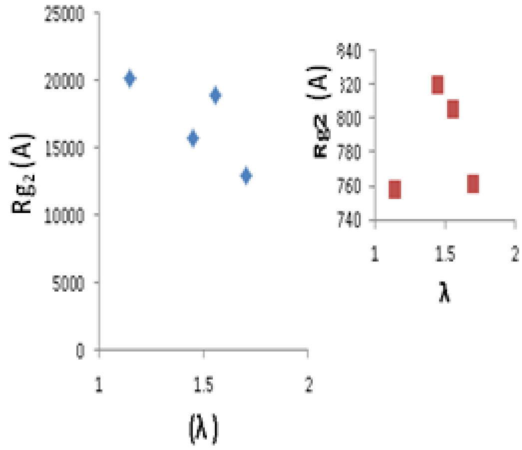

Figure 6. Variation in RG_1 and RG_2 (equation 1) with respect to the extension ratio, λ

5. Conclusion:

Electrically conductive Polyurethane nanocomposites with the 2% w/w MWCNT exhibited a conductivity of 3.28 x 10^{-5} s/m. The effect of uniaxial strain on the electrically conductive nanocomposite was studied. Remarkably, despite an extension ratio of 1.7 the overall electrical conductivity decreased slightly although fluctuations were observed under uniaxial strain. At the same time the measured SAXS data showed no alignment of the MWCNTs as might be expected from their aspect ratio. We interpret this as a consequence of the percolating network being formed from aggregates with some distributions in the size of those aggregates. The combination of strain coupled with in-situ SAXS measurements and accompanying electrical conductivity measurements has proved to be an effective tool to develop an understanding of these complex materials.

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